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## ***Chromium-bearing phases in the Earth's mantle: Evidence from experiments at 10-24 GPa and 1600°C***

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Phase relations in the SiO<sub>2</sub>–MgO–Cr<sub>2</sub>O<sub>3</sub> system were studied at 10–24 GPa and 1600 °C using a high-pressure split-sphere multi-anvil apparatus. We investigated the full range of starting compositions for the Mg<sub>4</sub>Si<sub>4</sub>O<sub>12</sub>–Mg<sub>3</sub>Cr<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> [1] and Mg<sub>2</sub>SiO<sub>4</sub>–MgCr<sub>2</sub>O<sub>4</sub> sections to derive *P*–*X* phase diagrams and synthesize chromium-bearing phases of a wide compositional range of the upper mantle, transition zone and lower mantle of the Earth. The phase assemblages include knorringite-rich (Knr) majoritic (Maj) garnet, Cr-bearing olivine/wadsleyite (Wad)/ringwoodite (Rgw), akimotoite (Ak)/bridgmanite (Brd), phases with calcium titanate-type structure, and anhydrous phase B. We report the new data on chromium incorporation in deep minerals, such as garnet, Wad, Rgw, Ak [2], and Brd [3].

Garnets synthesized in the MgO–SiO<sub>2</sub>–Cr<sub>2</sub>O<sub>3</sub> system are characterized by the high concentration of Si (>3 f.u.) and Cr (>90 mol % Knr). Cr incorporation in garnet may be illustrated by the scheme: Mg<sup>2+</sup>+Si<sup>4+</sup>=2Cr<sup>3+</sup>. All studied garnets (even those with the high Maj content) are cubic (*Ia* $\bar{3}d$ ) and show a decrease in cell parameters with increasing content of Maj: from *a* = 11.5879(2) Å (Knr<sub>90</sub>Maj<sub>10</sub>) to *a* = 11.457 Å (Knr<sub>3</sub>Maj<sub>97</sub>). Cr-bearing akimotoite (Ak) has an ilmenite-type structure, trigonal symmetry, and a structural formula (Mg<sub>1-x</sub>Cr<sub>x</sub>)(Si<sub>1-x</sub>Cr<sub>x</sub>)O<sub>3</sub> (where *x* = 0.015, 0.023, and 0.038). Cr incorporation in MgSiO<sub>3</sub>–Ak results in general increase of cell parameters (*a* from 4.7284(4) to 4.7380(1); *c* from 13.5591(16) to 13.5611(2) Å). Cr-bearing Brd synthesized at a pressure >20 GPa has the composition of (Mg<sub>1-x</sub>Cr<sub>x</sub>)(Si<sub>1-x</sub>Cr<sub>x</sub>)O<sub>3</sub>, where *x*=0–0.07, and the following cell parameters (for Cr-rich Brd, *x*=0.07): *a* = 4.8213(5), *b* = 4.9368(6), *c* = 6.9132(8) Å. Both Brd and Ak are characterized by the following scheme of Cr incorporation: Mg<sup>2+</sup>+Si<sup>4+</sup>=2Cr<sup>3+</sup>. Rgw has a spinel-type structure and, therefore, we suggest the following mechanism of Cr incorporation: 2<sup>VI</sup>Cr<sup>3+</sup>+<sup>IV</sup>Mg<sup>2+</sup>=2<sup>VI</sup>Mg<sup>2+</sup>+<sup>IV</sup>Si<sup>4+</sup>, which can be applied to Wad as well. Based on the composition of Wad, we may suggest an alternative mechanism of Cr incorporation in this phase: <sup>VI</sup>Cr<sup>3+</sup>+<sup>IV</sup>Cr<sup>3+</sup>=<sup>VI</sup>Mg<sup>2+</sup>+<sup>IV</sup>Si<sup>4+</sup>. In this case, we deal with the structure with Cr entering both tetrahedral and octahedral sites; this fact provokes almost the same unit-cell volumes. At 12–18 GPa we synthesized the phase with the composition of Mg(Mg,Cr)(Mg,Si)O<sub>4</sub> and distorted Ca-titanate structure (orthorhombic symmetry, *Cmc2*<sub>1</sub>). This phase is characterized by the high capacity for Si, in contrast to MgCr<sub>2</sub>O<sub>4</sub> with a Ca-titanate structure (orthorhombic symmetry, *Bbmm*), which is stable at a pressure of >18 GPa. As is evident from our data, incorporation of Cr in mantle phases decreases the pressure of the major phase transformations Ak/Brd, Ol/Wad, and Wad/Rgw by ~2 GPa (~70 km) in comparison with Cr-free phases.

Thus, our experiments simulate Cr-rich phase assemblages found as inclusions in diamond, mantle xenoliths, and UHP podiform chromitites. It is demonstrated that Cr incorporation in major mantle phases (garnet, Ak, and Brd) results in a strong increase in their cell parameters. Although our

experiments were performed in the simplified  $\text{SiO}_2\text{-MgO-Cr}_2\text{O}_3$  system and other components, such as Al, Fe, Ca, and Na may influence on the phase equilibria, it is believed that Cr exerts the significant control on phase relations, and the proposed trends should hold for more complex compositions.

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